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Processing and characterization of powdered silk micro- and nanofibers by ultrasonication

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ABSTRACT

Silk derived from *Bombyx mori* silkworm cocoons was degummed in an aqueous sodium carbonate solution, and the resulting silk fibroin fibers were placed in an acidic aqueous solution and were treated with ultrasonication to obtain powdered micro- and nanofibers. The morphologies and spectral characteristics of these powdered silk fibers were investigated in detail. The shape, surface and structural features of the powdered fibers were affected by the ultrasonic power and media. Increasing the acidity of the ultrasonic solution and increasing the ultrasonic power increased the fiber breakage speed, resulting in shorter fiber lengths. Powdered microfibers could not be obtained in a formic acid solution, while powdered nanofibers whose diameter below 1 μm were obtained in a combined formic acid and hydrochloric acid ultrasonication solution. Observation via SEM and optical microscopy revealed that the microfiber diameters were approximately 5–10 μm, and those of the nanofibers were approximately 30–120 nm. The analysis of laser sizer showed that the microfiber sizes ranged mainly from 20 to 100 μm. FT-IR and XRD spectra demonstrated that the relative amount of β-sheets increased after the ultrasonic treatment. The ε-amino group content on the surface of the micro- and nanofibers increased significantly. These studies provide reliable methods for the preparation of nano-scale silk fibroin fibers by ultrasonication and open new avenues for the development of powdered silk fibers as advanced functional biomaterials.

1. Introduction

Silk, a well-known natural fiber produced by the silkworm *Bombyx mori*, is composed of 5507 amino acids [1]. The biopolymer is made of both heavy and light chains [2]. The amorphous region comprises approximately one-third of the protein and primarily consists of the amino acid residues Phe, Tyr, and Try, which have large side groups. This region is responsible for the anti-UV radiation properties and hygroscopicity of the fibers. The crystalline portion makes up the remaining two-thirds of the protein and is largely composed of a repeated sequence of six residues $(Gly\text{-}Ala\text{-}Gly\text{-}Ala\text{-}Gly\text{-}Ser)_n$ that forms a β-sheet structure and is responsible for the mechanical properties of the silk fibers. Silk is a non-toxic, non-immunogenic and biodegradable natural protein. For thousands of years, it has been used as a high-grade raw material, and its popularity has increased over time. Silk fibroin, or regenerated silk fibers, has been utilized in surgical sutures due to its biocompatibility and degradability in the human body [3]. It has also been employed as a carrier for immobilized cells, enzymes or antibodies. Various forms of regenerated silk fibroin, including films and powders, have been used as biosensors and drug delivery materials, and they have been widely used in tissue engineering applications as 3D scaffolds, bionic blood vessels, cornea, food additives, and so on [3–5].

Silk proteins can be processed into various forms, such as powders, particles, gels, porous matrices, membranes or films, according to their application. Powdered silk has been extensively utilized for the surface modification of materials, cosmetics, health foods and industrial materials [7,8]. Silk powder, especially nanoscale powder, has a high binding affinity to medical materials due to its excess surface residue groups. It has been reported that powdered micro- and nanofibers have potential applications in manufacturing, as they can imitate the extracellular matrix composition and structure to provide an ideal environment for cell maturation [9,10]. Powdered silk with fine crystallinity is mainly obtained by mechanical processing and has a wide application potential in many fields [11,12]. However, crystalline silk particles have three drawbacks that could limit their utility: broad size ranges, larger particles and irregular morphologies. Further development of pulverized silk with finer crystallinity is restricted by current limitations in making finer particles of silk fibroin. Silk fibroin powders derived from liquid silk solutions using chemical processing via the addition of salts or alcohol are characterized by poor crystallinity, non-uniformity, irregular morphology and large sizes. There have been some studies on the powder as a vector for drug or enzyme immobilization [13,14]. Early in 2007, our group reported the fabrication of 35–125 nm-diameter spherical nanoparticles with fine crystallinity from regenerated liquid silk by means of water-miscible organic solvents [15] as a new potential vector for

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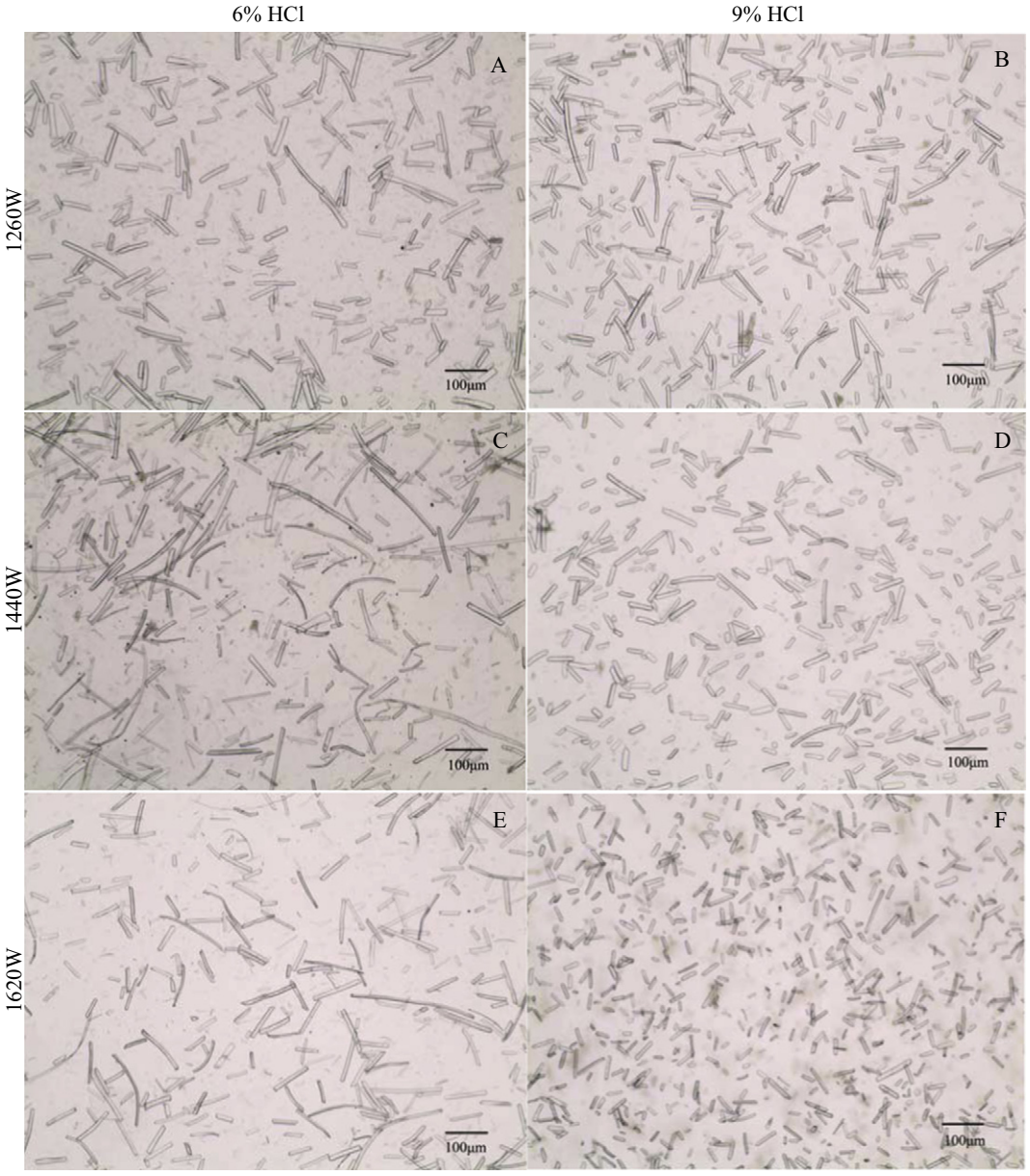

Fig. 1. Micrographs of silk fibroin fibers that resulted from varied concentrations of hydrochloric acid at different powers of ultrasonication. The diameter of the ultrasonic probe was 28 mm; ultrasonication was carried out for 5 h in the 6% HCl/1260 W system; ultrasonication was carried out for 4 h in the other systems. All the samples were sonicated with a silk fibroin concentration of 0.3% (w/v).

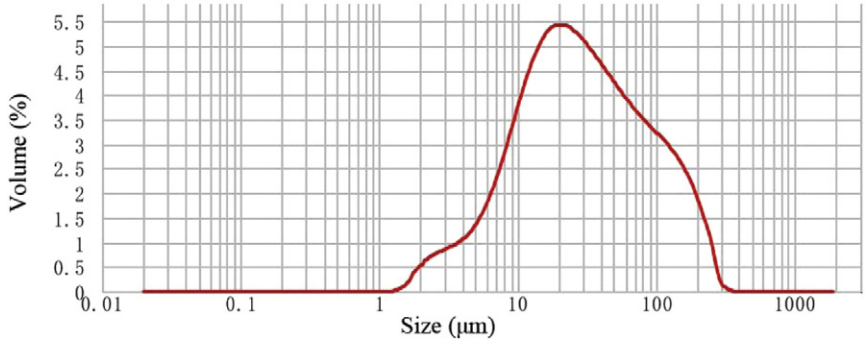

Fig. 2. Histogram-style analysis of powdered silk fibroin fiber size that resulted from 9% HCl/1620W system. The sample was sonicated with a silk fibroin concentration of 0.3% (w/v). The diameter of the ultrasonic probe was 28 mm.